Catalytic Activity of Calcium Oxide from Fishbone Waste in Waste Cooking Oil Transesterification Process

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Article Info

Abstract

Calcium oxide was obtained from waste fish bones that has been carried out systematically by decomposition at various temperatures that 800ºC, 900ºC and 1000ºC for 4 hours. Calcium oxide from the decomposition process was characterized using XRD, FTIR, SEM EDX and SAA. The result of XRD Diffractogram showed that the crystallinity increased as the calcination temperature increased. The absorption bands in the FTIR spectra of calcium oxide from calcined waste fish bones shown at 355 cm^{-1} region indicated Ca–O vibration, which was reinforced by the emergence of a peak at 859 cm^{-1}. Based on the analysis using SEM EDX, the calcined waste fish bones typically irregular particles and contained dominant calcium element. The low value of BET surface area and the total of pore volume were consistent with the adsorption measurement with SAA. The calcium oxide was applied for biodiesel synthesis from Waste cooking oil through transesterification reaction. The result of the optimization that the calcium oxide was decomposed from waste fish bones at 900ºC. It exhibited best catalytic activity in the transesterification of waste cooking oil providing maximum biodiesel yield of 93% at 4% (w/v) of catalyst loading. The decomposition of biodiesel are determined by GC MS that produced methyl palmitate, methyl linoleate, methyl elaidate, methyl linoleolate, methyl stearate and methyl linolenate.

INTRODUCTION

Biodiesel synthesis from waste cooking oil as an alternative energy source have been reported. Generally, biodiesel production via transesterification process used acid/base catalyst as well as enzyme. Catalyst activity in biodiesel production yield conversion of 98%, 99% and 91% for homogeneous base and acid catalyst and enzyme respectively (Mittelbach & Remschmidt, 2004). However, homogeneous catalyst is perfectly soluble in glycerol and partially soluble in biodiesel. Thus, separation process is needed to separate the catalyst from product and reactant which might increase operational cost. In order to solve this problem, transesterification process using heterogeneous catalyst need to be developed for more environmentally friendly, easy separation and reusable process.

Heterogeneous catalyst in waste cooking oil transesterification process have been used to reduce catalyst separation cost from mixture of product and reactant. Moreover, heterogeneous catalyst also has high catalyst activity. There are several heterogeneous catalysts that have been studied for waste cooking oil transesterification namely, oxides from metal transition, alkali metal and soil alkaline. Nevertheless, oxides from metal transition has acid alkalinity and produce low yield of biodiesel. Meanwhile, alkali metal and soil alkaline tend to have base alkalinity and produce higher yield of biodiesel (Mittelbach &

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Remschmidt, 2004). Metal oxides heterogeneous catalyst that commonly used in waste cooking oil transesterification process is calcium oxide (CaO). CaO is a strong base catalyst which is enviromentally friendly and has low solubility in methanol (Zabeti et al., 2009).

CaO is usually made by thermal decomposition of calcium salt such as $CaCO_3$, $Ca(OH)_2$, $Ca(C_2H_3OO)_2$ and CaC_2O_4. Cho et al., (2009) synthesizes CaO from $Ca(NO_3)_2$, $Ca(OH)_2$, $Ca(C_2H_3OO)_2$, $CaCO_3$, and CaC_2O_4 for tributyrin transesterification with methanol. The results showed that CaO from the decomposition of $Ca(OH)_2$ has 25 m^2g^{-1} surface area and yield 95% of biodiesel conversion. Ngamcharussrivichai et al. (2010) reported that limestone and its derivate were suitable as precursor in calcium oxide catalyst (CaO) production. Somehow, calcium oxide from dolomite has high catalytic activity compared to calcium oxide derived from limestone. The other calcium sources which can be used as precursor of CaO synthesis are bone wastes, such as chicken, fish, eggshell, and snail.

Development of CaO catalyst from waste sources has gained much attention from several researchers. Nakatani et al., (2009) used CaO from seashell waste for transesterification of soybean oil with methanol, the seashell waste in this research was calcined at 1000 °C. The biodiesel yield using this CaO catalyst was 96%. Viriyaempikul et al. (2012) utilized eggshell waste in transesterification of palm oil with methanol, the eggshell was calcined at 800 °C. The results showed that this catalyst gave 94% of biodiesel yield. CaO catalyst from animal bone has been used by Jazie et al., (2013) on transesterification of jatropha oil with methanol, this bones were calcined at 900 °C. The biodiesel yield in this process was 96%. Another works performed by Sirisomboonchai et al. (2015) showed that wasted scallop shell (Patinopecten yessoensis) able to catalyze transesterification process between used cooking oil with methanol, and gave 86% of biodiesel yield. The scallop used in here was calcined at 1000 °C. These previous studies showed that waste sea shell, egg shell and animals bone are potentially used as calcium oxide sources (CaO).

Fishbone wastes that can be obtained from fish fillet industries, fish flour industries or fish canning industries are potentially used as CaO sources. The waste of fish processing industries was obtained in the coastal area from the north of Pati,

Central Java. To date, the wastes of fish processing industry in Pati have not been used optimally, only being used as animal feeds. Tuna fishbone waste is a potential calcium source for calcium oxide production. The calcium inside fishbone can be found in the form of calcium salt and phosphor which is deposited in soft matrix structure consists of organic materials containing collagen and mucopolysacharide gel (Piliang, 2011). Conversion of calcium into calcium oxide is supposedly formed through thermal decomposition of $CaCO_3$ in fishbone.

MATERIALS AND METHOD

Materials

The materials used in this research were fishbone wastes which were obtained from the fisherman of the north coast in Pati, Central Java, waste cooking oil from fries sellers around UNNES Sekaran, natural zeolite from Bayah, Banten, and other materials, like HCl 37% (Merck), phenolphthalein, $H_2C_2O_4.2H_2O$ (Merck), KOH (Merck), Ethanol absolute (Merck), $(NH_4)_2CO_3$ (Merck), Methanol, Na_2SO_4 anhydrate (Merck), and n-Hexane grade for analysis (Merck).

Experimental Equipment

Equipment used in this research were OHAUS analytical balance PA214 analytical balance, oven memmert 854 schwabach, magnetic stirrer SSM 79-1, hot plate steroglass steromag, muffle furnace barnstead thermolyne 1400, centurion G.P. series, exciccator glaswerk wertheimgl 32, titration instruments set, reflux equipment set, X-Ray Difractometer type 6.000 Shimadzu, Fourier Transform Infra-Red type IR Prestige 21, Scanning Electron Microscopy type JOEL JSM 6510LA, Surface Area Analyzer type Quantachrome NOVA 1200e, Gas Chromatography type Agilent 6820, and Gas Chromatography Mass Spectrofotometer type Perkin Elmer Clarus 680 SQ 8T.

Experimental Procedure

The preparation of catalyst was carried out using decomposition method at high temperature based on the procedures stated by Farooq and Ramli (2015). Fish bones waste were boiled with aquadest for 30 minutes. Then, they were dried
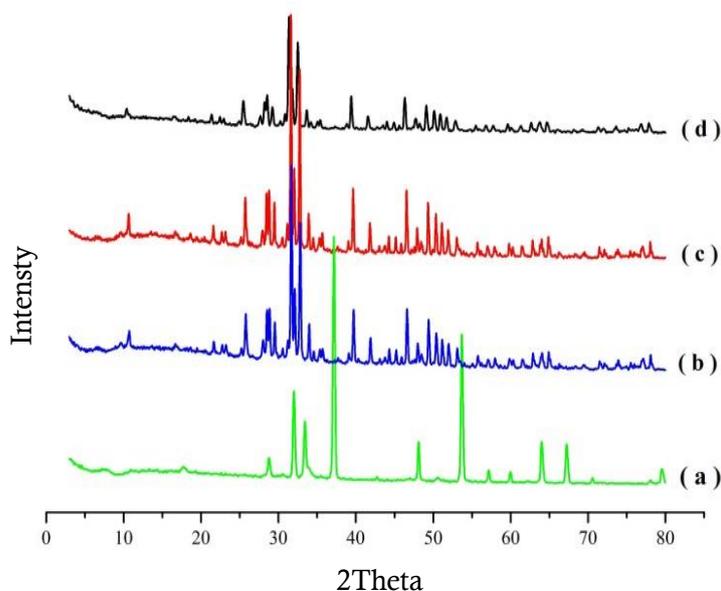
Figure 1. Diffractogram result of (a) standard calcium oxide (Merck), calcium oxide from decomposition of waste fishbone at (b) 800°C (c) 900°C and (d) 1000°C.

under the sunlight for 3 days. The dried fish bones waste were then macerated into powder and calcinated at 650°C for 8 hours. The formed catalyst was then soaked in 0.12 g/mL of ammonium carbonate solution for 24 hours to produce calcium carbonate. The deposits was then dried in the oven at 120°C until it dried. It was then calcinated using muffle furnace at the temperature of 800°C, 900°C, and 1000°C for 4 hours. The catalyst powder was then kept in the desiccator and characterized using XRD, FTIR, SEM, and SAA.

Waste cooking oil was prepared by purification method which is an adsorption process modified with the procedures performed by Yustinah & Hartini (2011). 200 mL of waste cooking oil was heated until the temperature of 100°C. 10 gram of activated natural zeolite was added into the heated waste cooking oil. The solution was stirred using magnetic stirrer for 60 minutes with the speed of 1,000 rpm. The mixture was then separated using filter paper. The determination of acid value in used cooking oil before and after the treatment were performed by using acid-base titration method according to the procedure of SNI 04-7182-2006 Dirjen Migas (AOCS Cd 3d-63).

The catalytic activities for transesterification of waste cooking oil were measured by performing batch-type reaction based on procedure carried out by Farooq & Ramli (2015). 20 mL of cooking oil was heated to the temperature 65°C. Next, 60 mL of methanol was added and followed

by addition of CaO catalyst 1%, 2%, 3%, 4%, and 5% w/v to the reactant volume. The mixture was stirred for 240 minutes with the speed of 300 rpm. Next, n-hexane was added into the mixture with 1:1 volume comparison to the mixture volume. Subsequently, mixture was then centrifuged to separate the biodiesel. 1% w/v of Na_2SO_4 anhydrate was added into biodiesel obtained from centrifugation process, GC analysis was then performed. Afterwards, biodiesel with optimum result was then identified its chemical compounds using GC-MS.

RESULTS AND DISCUSSIONS

Calcium oxide (CaO) from fishbone waste was obtained through thermal decomposition at 800°C, 900°C, and 1000°C for 4 hours (Farooq & Ramli, 2015). Calcination process was conducted at high temperature to make sure that all fishbone have been perfectly decomposed into CaO. Calcium oxide in the catalyst of the synthesis was then characterized using XRD, FTIR, SEM EDX, and SAA.

The purpose of XRD analysis is to determine the crystallinity of synthesized calcium oxide catalyst. The diffractogram of catalyst is shown in Figure 1.

In Figure 1, the diffraction lines of calcium oxide (CaO) located at 32.221°, 53.890° and 64.122° which is in accordance with calcium oxide standards from JCPDS Number 01-077-2376.
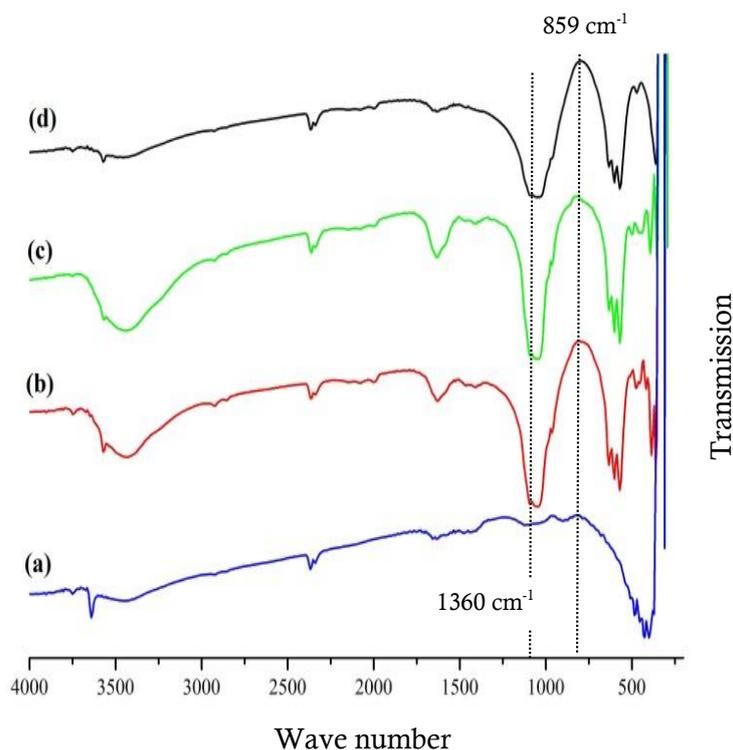
Figure 2. IR spectrum of (a) standard calcium oxide (Merck), calcium oxide from decomposition of waste fishbone at (b) 800°C (c) 900°C and (d) 1000°C.

Nevertheless, other unexpected compounds such as $CaCO_3$ and $Ca(OH)_2$ were found at diffraction line of 28.911°, 43.830° and 48.056°. The existence of $CaCO_3$ in the catalyst shows that $CaCO_3$ and $Ca(OH)_2$ were not fully converted into CaO and H_2O. As stated by Hu et al. (2011) that the existence of $CaCO_3$ in the catalyst was caused by imperfect calcination process in converting $CaCO_3$ to be calcium oxide. While, $Ca(OH)_2$ was formed due to hygroscopic properties of CaO and also it easily reacted with H_2O from the air after calcination process. The presence of $Ca(OH)_2$ can be seen in 2θ = 25,852°, 34,035°, 46,668°, and 50,460°. Figure 1 also shows that the diffractogram intensity is getting stronger as the increase of calcination temperature. The increasing of diffractogram intensity shows that CaO has higher crystallinity. It is in line with the statement from Farooq and Ramli (2015) that the increment of catalyst structure crystallinity will increase diffractogram intensity. Catalyst with higher crystallinity will have higher catalytic activity and porosity.

FTIR analysis is used to analyze the functional groups in a certain material either organic or non-organic compound. FTIR spectra of non-organic material commonly appears at 1500 cm^{-1} region. Synthesized CaO has an FTIR spectra

at wavenumber of 1000 cm^{-1} since this is an ionic compound. IR Spectrum of the catalyst is presented in Figure 2.

Figure 2 shows the existence of CaO in the synthesized catalyst. The absorption bands in the FTIR spectra of calcium oxide from calcined waste fish bones shown at 355 cm^{-1} region indicated Ca–O vibration, which was reinforced by the emergence of a peak at 859 cm^{-1}. The O-C-O stretching peak is located at the wave number between 1381 cm^{-1} to 1636 cm^{-1}. However, higher calcination temperature will decrease the amount of $CaCO_3$ shown by the decrement of vibrational spectra of carbonate ion. Presence of carbonate ion is caused by high concentration of CaCO3 compounds which has not been decomposed into CaO. The peaks appear between 3418 - 3449 cm^{-1} attributed to the –OH group, where –OH group with sharp peaks shows the characteristics of calcium oxide (Ruiz et al., 2009). The sharp band at 3750 cm^{-1} might be as a result of an absorbed molecule of water on the surface of calcium oxide. It is due to hygroscopic characteristic of calcium oxide and also calcium oxide can absorb water vapor from the air easily (Jazie et al., 2013).

Figure 2 also shows that the existence of PO_4^{3-} group in the synthesized calcium oxide
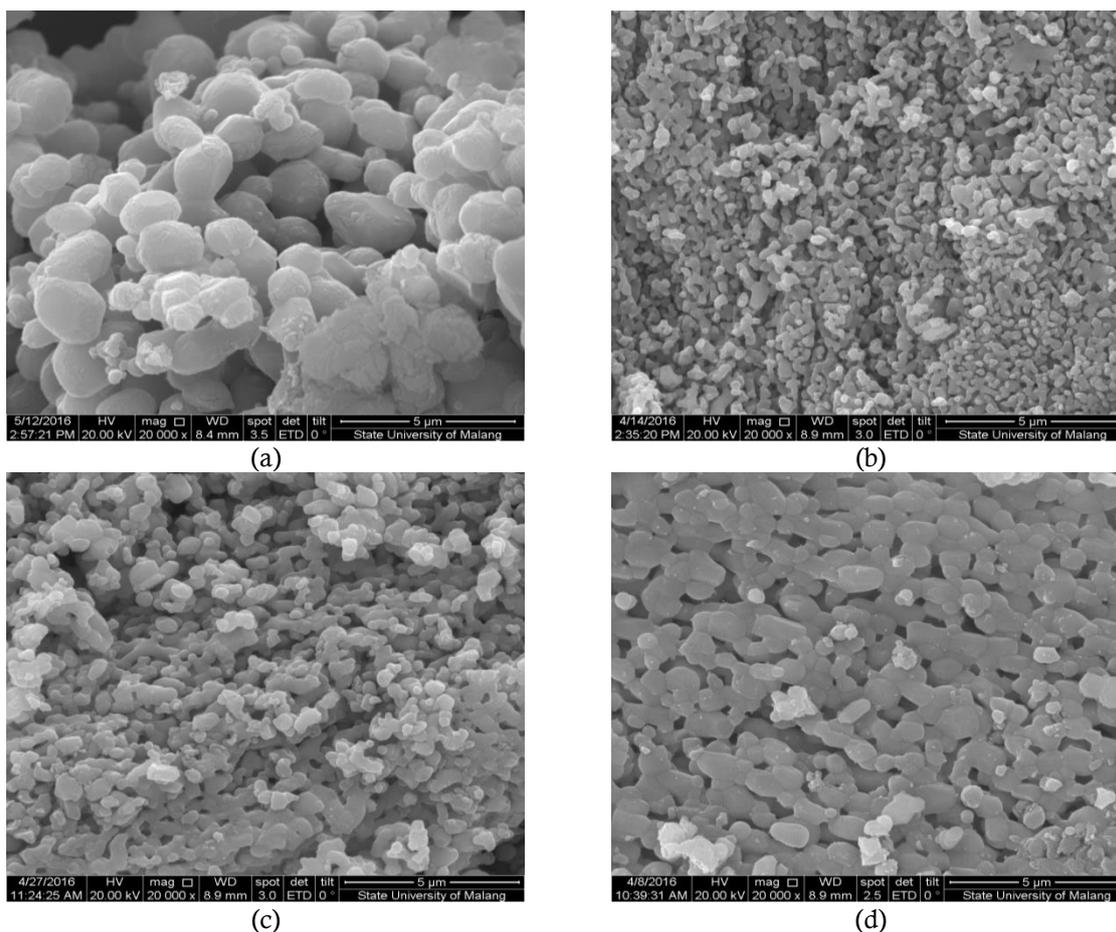
Figure 3. SEM images with 20,000x magnification of (a) standard calcium oxide (Merck), calcium oxide from decomposition of waste fishbone at (b) 800°C (c) 900°C and (d) 1000°C.

nonetheless it peak does not appear in the sample of standard calcium oxide from Merck. First asymmetrical stretching vibration of $-PO_4^{3-}$ is found at the band between of $1049 - 1042$ cm^{-1}. While the second band was found between wave number of $1088 - 1096$ cm^{-1}. From all three samples of synthesized calcium oxide, the peaks at 571, 602 and 633 cm^{-1} were attributed to the Ca^{2+} group. According to Farooq & Ramli (2015) PO_4^{3-} and Ca^{2+} group are the basic material of (β-$Ca_3(PO_4)_2$) with pores on the surface.

SEM analysis was performed to study the surface morphology of synthesized calcium oxide catalyst. The SEM result of synthesized catalyst can be seen in Figure 3.

Figure 3 shows the uniform morphology of calcium oxide catalyst. The higher calcination temperature resulted bigger particle size. Besides that, it also influence the conversion of $CaCO_3$ into CaO and produce uniform catalyst distribution. Madhu et al. (2014) explained that the calcination temperature from 800°C to 1000°C can eliminate the organic components like fats and proteins and

increase the surface area of catalyst pores. The elimination of fats and protein are shown by color change of the catalyst. As the increase of calcination temperature catalyst color become whiter. Physical appearance of whitened CaO is shown in Figure 4.

The EDX analysis was carried out to show emphasize the components contained in the catalyst. This unsure components was not analyzed as oxide compound. The EDX analysis results are shown in Figure 5.

In Figure 5 the percentage of calcium oxide in the catalyst was ranged from 40.78 % to 48.46%, while its oxidant in the form of CaO has percentage of 57 to 62%. Phosphor was not found at the analyzed CaO standard meanwhile phosphor oxide appeared in the decomposed fishbone waste catalyst in the range of 20 to 22%. Phosphor as the main component of bones might be the reason of phosphor existence in the EDX result, this phosphor was not decomposed perfectly and appear in the result analysis (Schubert & Husing, 2000).

The surface area analysis of the catalyst was carried out by using adsorption/desorption of

Figure 4. Physical appearance of synthesized catalyst from (a) standard calcium oxide (Merck), calcium oxide from decomposition of waste fishbone at (b) 800°C (c) 900°C and (d) 1000°C.
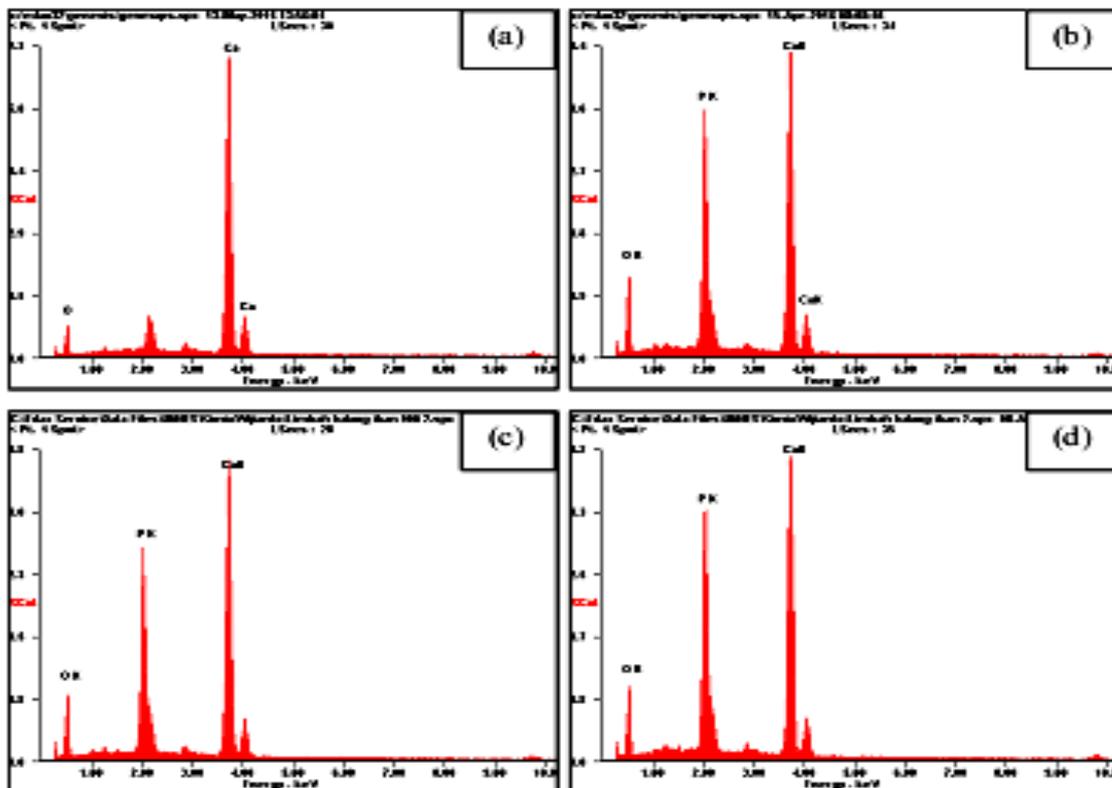
Figure 5. EDX analysis of (a) standard calcium oxide (Merck), calcium oxide from decomposition of waste fishbone at (b) 800°C (c) 900°C and (d) 1000°C.

Nitrogen using Surface Area Analyzer (SAA). BA method was used to measure the surface area. The specific surface area and total pore volume of the catalyst at different calcination temperature are shown in Table 1.

BET studies confirmed that the specific surface area decreased as the calcination temperature increase from 800 to 1000°C. Higher calcination temperature increase the pore size and broke the crystal structure of synthesized calcium oxide. This is in accordance with Lee et al. (2014)

statement where the increase of calcination temperature produce catalyst with bigger crystal size and smaller surface area.

The characterized calcium oxide was then applied in transesterification process of waste cooking oil. Waste cooking oil preparation was adsorption and filtration process. Adsorption process was performed by using activated natural zeolite to eliminate free fatty acid and remove dissolved dyes in waste cooking oil. The purpose of filtration process was to separate the oil from dirt

Tabel 1. Specific surface area and pore volume of catalyst

Catalyst type	Specific surface area (m^2/g)	Pore volume (cc/g)
Standard calcium oxide	79.4169	1.3700×10^{-2}
Calcium oxide 800ºC	64.7152	0.9734×10^{-2}
Calcium oxide 900ºC	43.8241	0.6775×10^{-2}
Calcium oxide 1000ºC	13.3907	0.3066×10^{-2}
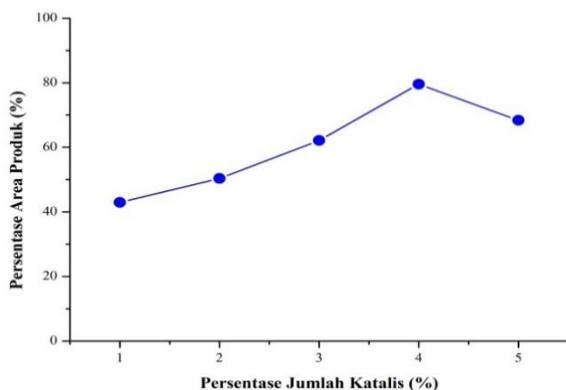
Figure 6. Product percentage area as a function of catalyst amount (w/v)
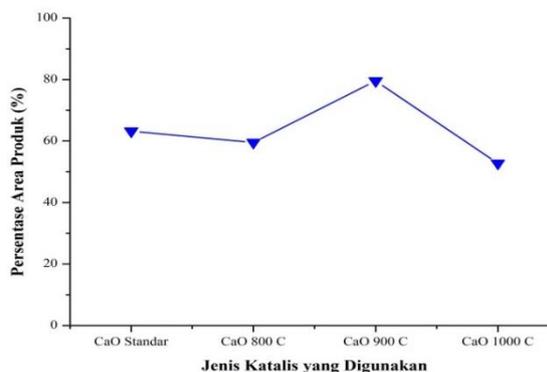
Figure 7. Optimization result of catalyst type

and adsorbent. Adsorption process of waste cooking oil was successfully decrease the acid number from 2.5686 mg KOH/g to 0.3412 mg KOH/g. The decrease of acid number is caused by the adsorbed free fatty acid in oil using zeolite through van der walls bond.

Methyl ester was produced from trans-esterification of triglyceride in waste cooking oil with methanol in the presence of calcium oxide catalyst. The optimization was carried out to the catalyst percentage (w/v) and catalyst type. The optimization result of catalyst amount percentage (w/v) and catalyst type are presented in Figure 6 and 7.

Figure 6 shows that the optimum condition was found at 4% catalyst amount percentage, while the product area percentage is decreasing in the 5% addition of catalyst. The decrease of percentage from the products area in the use of 5% catalyst shows that there is a problem in the collision between molecules because the catalyst was deposited and thickened in three-neck flask. Wendi et al., (2015) reported that the number of catalyst make the obstruction of contact between oil and methanol resulting the decrease of biodiesel conversion on the 3% to 4% catalyst amount percentage. The decrease of biodiesel conversion was also caused by the reaction between catalyst and oil which blocked the contact between oil and methanol. This will decrease the reaction rate of

methanol and oil (Arita et al., 2008). Setiowati et al. (2014) also stated that the biodiesel conversion decreases when there are too much catalyst involved in the reaction. Too many catalyst will produce emulsion from saponification reaction. This resulted thicker mixture which require more energy consumption for mixing process. Catalyst deposition in the transesterification process lead to the decrease of calcium oxide catalytic activity, thus as the decrease of catalyst active sites, it will disturb the adsorption process of reactant molecules on the catalyst surface (Farooq & Ramli, 2015).

Figure 7 shows the effect of catalyst type to the product area percentage. The commercial CaO without calcination has 65% of product area percentage. While CaO from waste fishbone with calcination at 800°C has lower product area percentage compared to commercial CaO without calcination. Highest product area percentage obtained from CaO with calcination process at 900°C and the product percentage is decreasing at the usage of CaO with calcination temperature at 1000°C. The decrease of Product area percentages at CaO with calcination process at 1000°C was caused by sintering in calcination process which use very high temperature. This leads to a smaller catalyst surface area (Viriya-empikul et al., 2012). Figure 6 also shows that commercial CaO which has largest specific surface area has lower catalytic activity than CaO catalyst with calcination
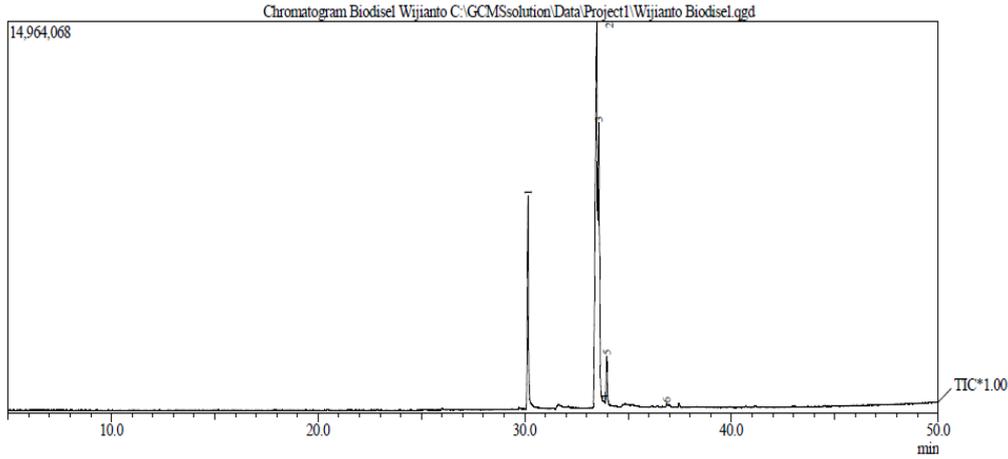
Figure 8. GC chromatogram of the optimized biodiesel

Tabel 2. Physical properties of the optimized biodiesel with testing methods

No.	Properties	Optimized Biodiesel	Biodiesel Standard ASTM	Biodiesel Standard SNI
1.	Density at 40°C	0.871	-	0.840 – 0.920
2.	Kinematic viscosity at 40°C (cSt)	2.5	1.9 – 6.0	2.3 – 6.0
3.	Flash point (°C)	96 °C	Min. 130	Min 100
4.	Cloud point (°C)	24 °C	Max. 26	Max. 26

temperature of 900°C. In this case, catalyst surface area does not affect catalyst activity very much. In contrary with statement of Lesbani et al. (2015) where catalyst with smaller surface area has smaller contact with reactant molecules. Therefore, it will produce biodiesel with smaller yield and also decrease the catalyst activity. The low catalyst activity of CaO might be caused by late response of regeneration process. Water molecules from air can blocked the catalyst pore, since CaO has high reactivity towards water vapor in the air. Somehow, the result of this research is in line to the research of Boro et al. (2011) which use catalyst of CaO 900 °C from shell waste of *Turbonilla striatula*. The transesterification palm oil using this catalyst process produced 93% of biodiesel.

The biodiesel as a result of transesterification process was then characterized using GC MS to study the methyl ester components. Figure 8 shows the chromatogram results of biodiesel using GC MS. The chromatogram shows six peaks. The first peak with 30.156 minutes retention time has area percentage of 16.25% indicated the presence of methyl palmitate. Second peak with 33.482 minutes of retention time has 50.12% area percentage indicated methyl linoleate. Third peak was methyl elaidate found at 33.579 minutes retention time with area percentage of 33.579%. Fourth peak with

33.850 minutes retention time has 0.53% area percentage indicated methyl linoleate. Fifth number with retention time of 33.963 minutes and area percentage of 3.43% indicate the presence of methyl stearate and the sixth peak found at retention time of 36.866 minute with area percentage of 0.38% indicate methyl linoleate.

GC-MS chromatogram result from optimized biodiesel shows relatively high percentage of methyl ester formation. It shows that calcium oxide from the decomposition of fishbone waste can be used as a catalyst for biodiesel production.

Biodiesel physical properties of biodiesel was conducted to study the similarity between optimized biodiesel and biodiesel standard from ASTM and SNI (Indonesian Standard). The biodiesel properties can be found in Table 2.

The biodiesel physical data properties optimization process shows that the result is in line with the standard of biodiesel properties as stated in ASTM D 6751 and SNI from Dirjen Migas (National Directorate of Oil and Gas). Nonetheless, the flash point from optimized biodiesel has lower value compared to the result from SNI and ASTM. This low flash point is possibly caused by the lower amount of methyl ester found in the synthesized biodiesel rather than in the standard biodiesel.

CONCLUSION

Catalytic activity of calcium oxide that was decomposed from waste fish bones in transesterification process of waste cooking oil has been tested. The best catalytic activity which provide the highest yield was found at calcination temperature of 900°C, catalyst addition percentage of 4% (w/v), waste oil to methanol volume ratio of 1:3, reaction temperature of 65°C and reaction time of 240 minutes. The results compositions were 16.25% of methyl palmitate, 50.12% methyl linoleate, 29.29% methyl elaidate, 0.53% methyl linoleolate, 3.43% methyl stearate and 0.38% methyl linolenate. Physical properties of synthesized biodiesel at its optimum condition were having density of 0.871 g/mL at 40°C, kinematic viscosity of 2.5 cSt at 40°C, flash point of 96°C and cloud point at 24°C that have been measured based on ASTM D 6751 and SNI 04-7182-2006 Dirjen Migas.

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